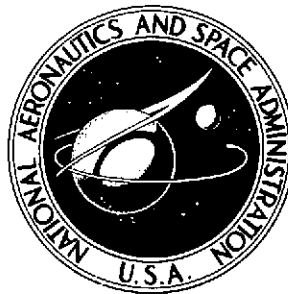


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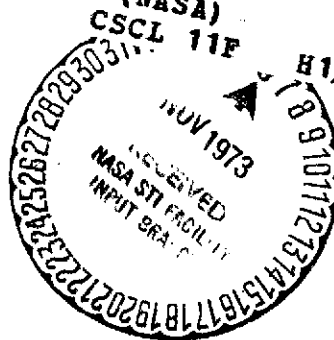
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AUGER ELECTRON SPECTROSCOPY STUDY
OF INITIAL STAGES
OF OXIDATION IN A COPPER -
19.6-ATOMIC-PERCENT-ALUMINUM ALLOY

by John Ferrante

Lewis Research Center

Cleveland, Ohio 44135

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AUGER ELECTRON SPECTROSCOPY STUDY OF INITIAL STAGES OF OXIDATION IN A COPPER - 19.6-ATOMIC-PERCENT-ALUMINUM ALLOY

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SUMMARY

Auger electron spectroscopy was used to examine the initial stages of oxidation of a polycrystalline copper - 19.6-atomic-percent-aluminum alloy. The growth of the 55-eV "aluminum oxide" peak and the decay of the 59-, 62-, and 937-eV copper peaks were examined as functions of temperature, exposure, and pressure. Pressures ranged from 1×10^{-7} to 5×10^{-4} torr of O_2 . Temperatures ranged from room temperature to $700^\circ C$. A completely aluminum oxide surface layer was obtained in all cases. Complete disappearance of the underlying 937-eV copper peak was obtained by heating at $700^\circ C$ in oxygen at 5×10^{-4} torr for 1 hour. Temperature studies indicated that thermally activated diffusion was important to the oxidation studies. The initial stages of oxidation followed a logarithmic growth curve $\left[x = x_0 \ln \left(1 + \frac{t}{\tau_0} \right) \right]$ with a pre-logarithmic factor, x_0 , of 0.119 (thickness in arbitrary units) and a time factor, τ_0 , of 0.129 second.

INTRODUCTION

The formation of oxide layers for corrosion protection has long been a topic of interest (refs. 1 to 7). The principal objective of such studies was to fabricate alloys in which one component was selectively oxidized on the surface. This single component oxide was to be chemically inert (as, for example, aluminum oxide) and thus prevent further oxidation of the surface. The oxide surface film could have other desirable properties such as prevention of hydrogen embrittlement in titanium-aluminum alloys and altering friction and wear behavior of surfaces.

Until recently, no analytical technique has been available to identify the initial stages of oxidation of pure metal and alloy surfaces. The most frequently used techniques have been weight change, hot-stage X-ray diffraction, and hot-stage high-energy

electron diffraction (ref. 1). These techniques, however, do not have sufficient depth resolution to detect the initial stages of oxidation. In the past few years, a new experimental technique, Auger electron spectroscopy (AES), has been developed. It is described in references 8 and 9. This technique provides an elemental analysis of the top one to five layers of a crystal surface and may aid in understanding oxidation of pure materials and the selective oxidation of alloy surfaces. Some studies of alloy oxidation have been attempted with the use of AES on the alloy Nimonic 80 (ref. 10). These studies were preliminary in nature and were conducted on complicated multicomponent systems. The AES technique has an additional advantage in examining oxidation in that with some elements the location of the Auger peak will shift in energy with chemical compound formation (an effect known as the "chemical shift" (ref. 8) of the peak). This shift allows unequivocal identification of oxide formation on the surface. In fact, the two materials of most interest in corrosion studies, aluminum and silicon, undergo very large chemical shifts, which makes the detection of the oxides of these materials extremely easy. The location of the aluminum AES peak shifts from 70 to 55 eV as a result of oxide formation (ref. 11). Henceforth in the report, the shifted aluminum peak will be referred to as the "aluminum oxide" peak.

The present report examines the oxidation of a copper - 19.6 atomic-percent-aluminum alloy. The sample studied is polycrystalline. The purpose of the report is to present procedures for performing quantitative oxidation studies of the alloy with the use of AES at low oxygen pressures (10^{-7} to 10^{-4} torr), and to determine whether some model for oxidation is consistent with the empirical results. In the report, studies of temperature effects, pressure effects, diffusion, and relevance to specific models are examined.

APPARATUS

The AES vacuum system for performing these studies is shown schematically in figure 1. The stainless-steel system is bakeable to 250°C . The system is sorption-, sublimation-, and ion-pumped and attains a base pressure of 10^{-11} torr.

The sample could be rotated for AES studies and ion bombardment cleaning. The alloy was heated by electron bombardment in order to avoid effects on the AES results caused by high direct-current heating (ref. 12). Temperatures were measured by a Chromel-Alumel thermocouple spot-welded to the bottom of the specimen, which was a cylinder approximately 1 centimeter in diameter and 0.5 centimeter thick.

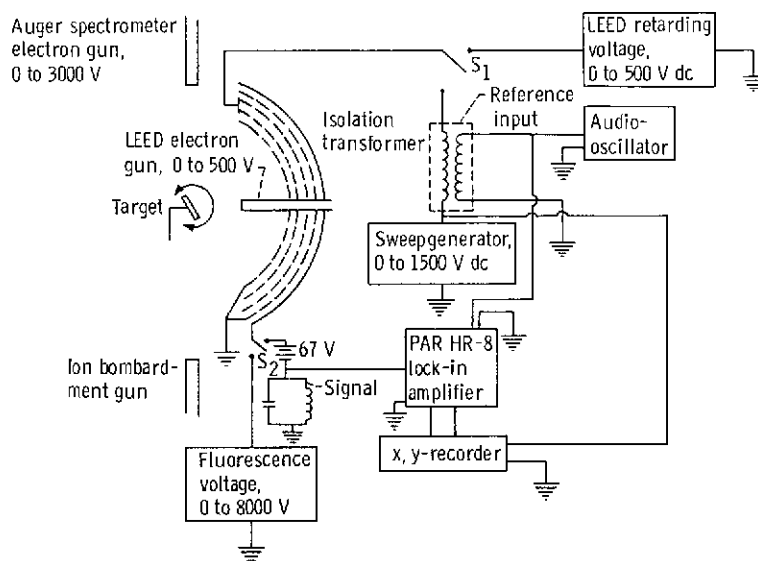


Figure 1. - Schematic of the AES system.

MATERIALS

The copper - 19.6-atomic-percent-aluminum alloy studied was fabricated by mixing pieces of copper and aluminum, each having impurity contents of less than 10 parts per million. The materials were then heated at 1150°C in a carbon crucible placed in an induction furnace to form the alloy, which was then cooled slowly. The oxygen and argon gases used in the study were research grade, with impurity contents less than 100 parts per million.

The sample was cut from the slug with a string saw. It was then polished on silicon carbide paper to 600 grit. It was given a final polish with 3 - micrometer diamond paste. Following polishing, the sample was electro-polished in an orthophosphoric acid electrolyte.

PROCEDURE

Specimen Cleaning

After it was mounted in the vacuum system, the specimen was outgassed to the point where the pressure in the system could be maintained at approximately 10^{-10} torr when heated to 500°C . Following outgassing, the alloy was cleaned by sputtering with argon ions at a beam energy of 400 eV and a current density of approximately 0.5×10^{-6} ampere per square centimeter. The sputter-cleaned surface was then annealed at 400°C . This

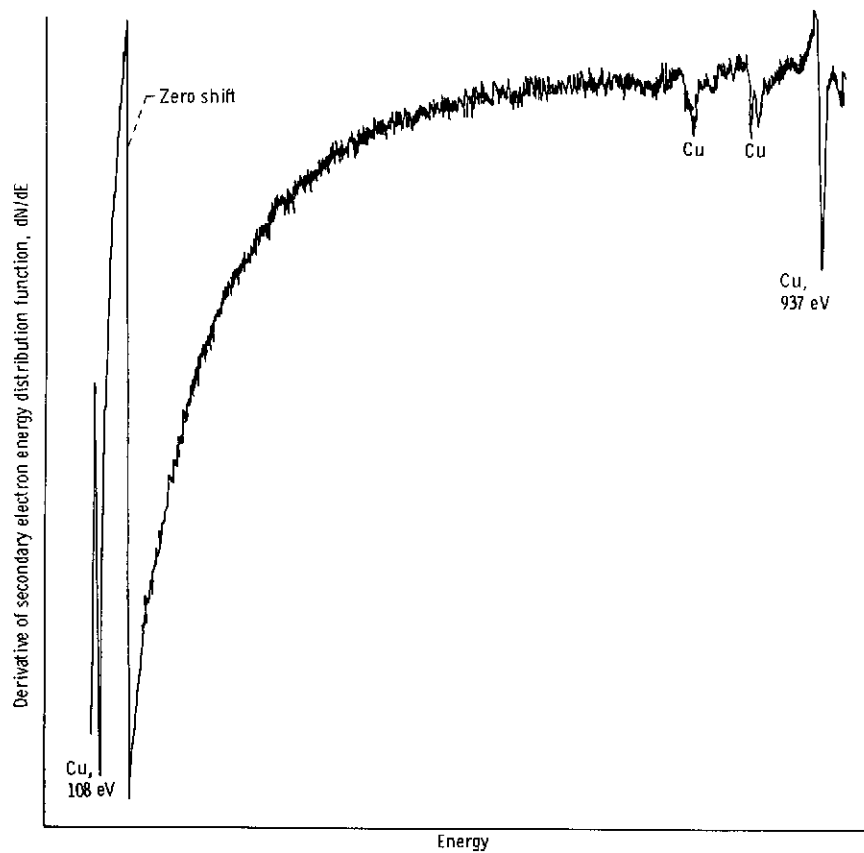


Figure 2. - Example of AES trace from clean copper - 19.6-atomic-percent-aluminum alloy. (Energies ranging from 100 to 950 eV.)

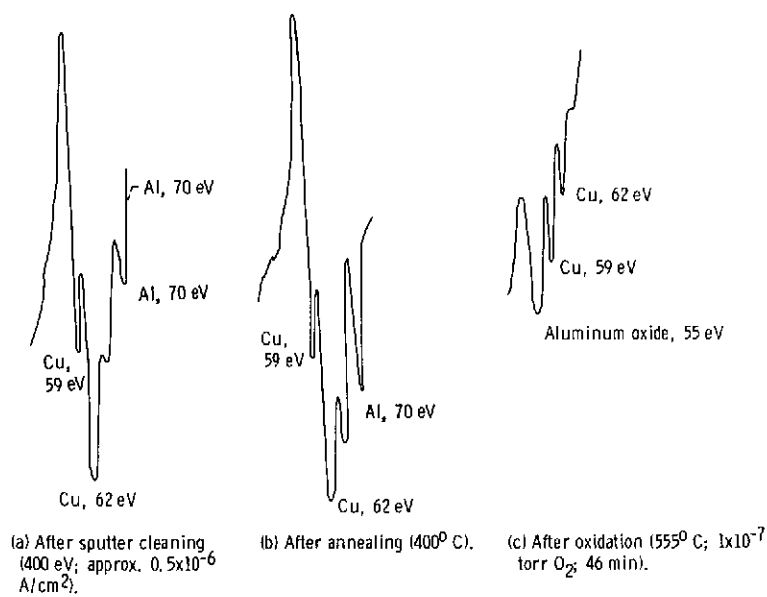


Figure 3. - Low-energy AES spectrum.

procedure resulted in the "clean" spectrum in the 100- to 950-eV range shown in figure 2. Figures 3(a) and (b) show the AES spectrum in the 40- to 80-eV range following sputter cleaning and following annealing, respectively. Note the increase in the aluminum AES peak-to-peak height, which indicates that segregation (refs. 13 and 14) has occurred during the annealing.

Oxidation Studies

In the oxidation studies, the sample was heated in oxygen at pressures ranging from 1×10^{-7} to 5×10^{-4} torr and at temperatures ranging from 250° to 700° C. At the three lowest pressures, the low-energy copper, aluminum, and aluminum oxide AES peaks were monitored as functions of time. The 937-eV copper AES peak was also monitored as a function of time for a pressure of 5×10^{-6} torr and a temperature of 550° C. The 100-eV copper peak was examined along with the low- and high-energy copper peaks in order to investigate electron attenuation effects. In order to establish the effects of heating at elevated temperatures on the quantity of oxygen in the surface region, the (520 eV) oxygen AES peak was recorded as a function of time for exposure at a pressure of 5×10^{-6} torr at room temperature and at 500° C. To determine the effects of metal ion diffusion, the oxygen was pumped out after a long exposure at 550° C and 5×10^{-6} torr, and the 937-eV copper peak and the free-aluminum peak were observed as functions of time. A discussion of the location of the copper AES peaks can be found in reference 15 and of the aluminum AES peak and its chemical shift in reference 11. Figure 3(c) gives an example of the chemical shift of the aluminum AES peak as a result of combination with oxygen. For all oxygen pressures except 5×10^{-4} torr, oxygen was introduced into the vacuum system by a variable-leak valve while the ion pump was operating. A given pressure was obtained by balancing the oxygen leak rate against the pumping rate. To obtain a pressure of 5×10^{-4} torr, the pump was turned off and the system was bled up to the pressure with the variable-leak valve.

The purity of the oxygen environment was checked with a quadrupole mass spectrometer. The principal contaminant was carbon monoxide. The ratio of the oxygen peak height to the carbon monoxide peak height could be maintained at greater than 50 by argon instability treatments of the pump (ref. 16).

Data Reduction and Operating Conditions

The data were reduced by measuring the peak-to-peak height of the corresponding AES peaks. The AES peak heights were normalized in order to eliminate effects of sensitivity changes from one run to the next. All of the low-energy peaks were normalized by dividing by the peak-to-peak height of the 59-eV copper peak obtained after the alloy

had been sputter-cleaned and annealed. The oxygen peak was normalized by dividing by the clean, annealed, 937-eV copper peak-to-peak height. All peaks were also normalized by dividing by changes in the total collected current to account for current changes resulting from the presence of oxygen. The data were then plotted as a function of time.

Typical lock-in amplifier settings during the runs were 2 millivolt sensitivities and 100 millisecond time constants. Modulation voltages of 8 volts peak-to-peak were used at AES energies above 100 eV, and 2 volts peak-to-peak at energies below 100 eV. Typical sweep times were 100 volts per minute above 100 eV, and 25 volts per minute below 100 eV. The AES electron beam energy was 2500 eV.

RESULTS AND DISCUSSION

In the INTRODUCTION, it was stated the oxides of aluminum and silicon could be identified unequivocally because of chemical shifts in the position of the AES peaks. Figure 3 shows that the position of the aluminum AES peak has shifted from an energy of 70 eV (fig. 3(b)) to an energy of 55 eV (fig. 3(c)). As stated earlier, this 55-eV aluminum peak will be called the "aluminum oxide" peak. Note that all low-energy peaks are clearly resolved. It is not possible to distinguish the oxides of copper, since the chemical shifts on oxide formation (if any) are too small.

Evidence for a Purely Aluminum Oxide Film on the Surface

The intent of this report is to examine the initial stages of oxidation of alloys by AES. To do this, it is necessary to have some techniques for establishing the composition of the growing film. There are a number of possibilities for the composition of the surface film. It can be a combination of oxides, a combination of oxides and free metals, or a single oxide coating. An important result of this study is the determination of the nature of this film in the early stages of oxidation.

In order to demonstrate that only an aluminum oxide film has formed, copper peaks are used as probes to determine the nature of the film. It is necessary to have complete disappearance of the copper peaks in the Auger spectrum, at some stage, to demonstrate that there is a purely aluminum oxide film covering the surface. Figure 4 shows the results of attempting to examine this possibility. The alloy was heated at 700° C in oxygen at 5×10^{-4} torr for 1 hour. As can be seen, the 937-eV copper peak disappeared completely into the background noise, which indicates the formation of a completely aluminum oxide surface film. It seems reasonable to conclude, therefore, that an aluminum oxide surface film is forming during the initial stages of oxidation.

To have an indication of the nature of the film when complete disappearance of the

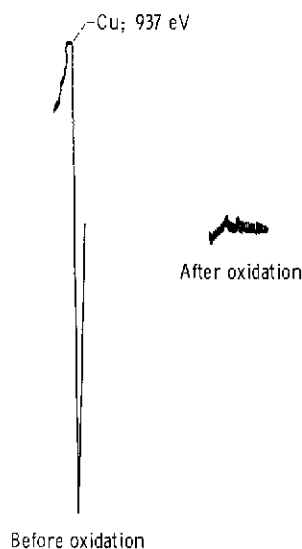


Figure 4. - Disappearance of 937-eV copper AES peak as a result of oxidation by heating at a temperature 670° to 700° C for 1 hour in an oxygen atmosphere of 5×10^{-4} torr.

copper peaks has not occurred, the energy dependence of the attenuation of the copper peaks may be used (ref. 14). If an aluminum oxide film is covering the copper-aluminum substrate, then more energetic electrons should be able to penetrate a thicker layer than less energetic electrons and, therefore, the peak height should be attenuated less for the 937-eV copper electrons than for the 59-eV copper electrons. Figure 5 shows examples of this attenuation for the 59-eV electrons. Examination of the energy dependence of the copper AES peaks after heating for approximately 1 hour at 510° C in oxygen at 5×10^{-6} torr indicated that the 59-eV copper peak was attenuated by a factor of 100, the 108-eV copper peak (not shown) by a factor of 20, and the 937-eV copper peak (not shown) was attenuated by a factor of 4. Therefore, the attenuation of the copper peaks had the correct energy dependence for an aluminum oxide film covering the copper-aluminum substrate.

At this point it should be noted that in all conditions examined during oxidation, ranging from room-temperature adsorption to oxidation at elevated temperature, the free aluminum peak at 70 eV disappeared completely. This fact indicates that in all cases, an aluminum oxide surface film was formed. The disappearance of the free aluminum peak for room temperature adsorption supports the previous observation of surface segregation of aluminum (fig. 3 and refs. 12 and 13). This result may also indicate that surface segregation could be a contributing factor in the selective oxidation. Also, since the free aluminum peak was never observed during oxidation, the results show no evidence for island formation. However, it is conceivable that the oxide film was nonuniform.

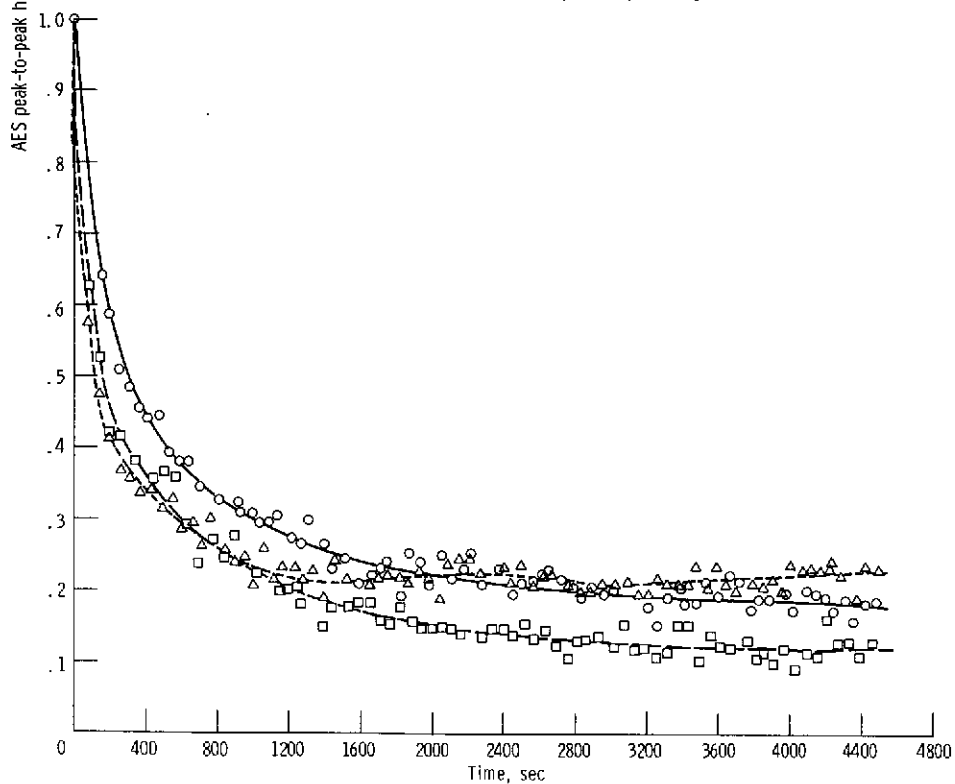
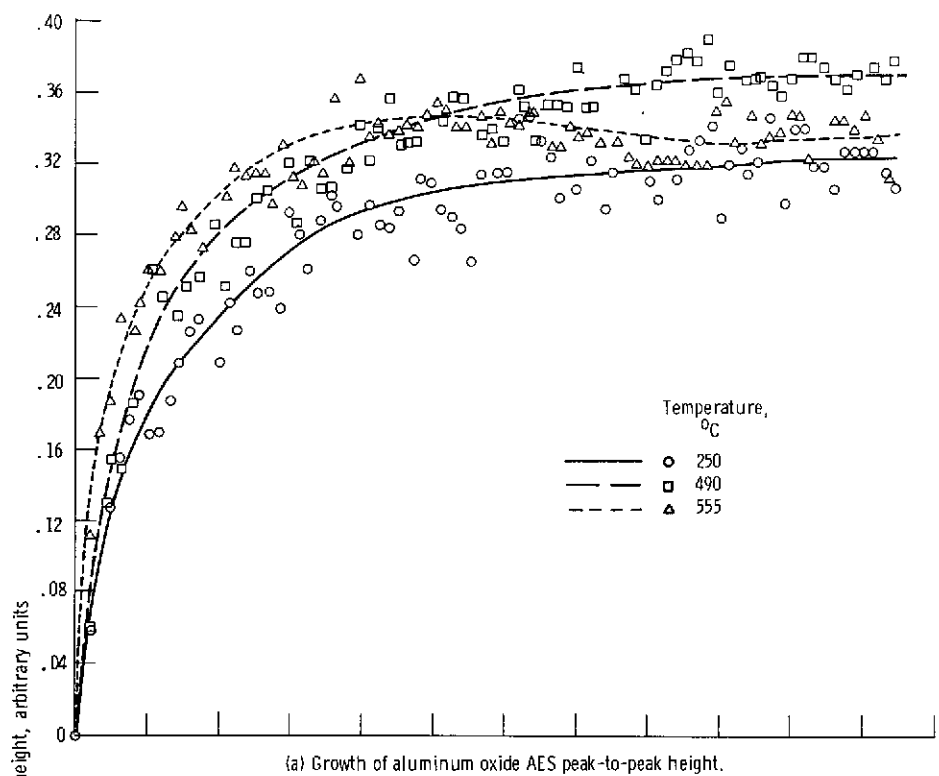


Figure 5. - Oxidation of copper-aluminum alloy at 1×10^{-7} torr at various temperatures as a function of time.

Temperature Effects

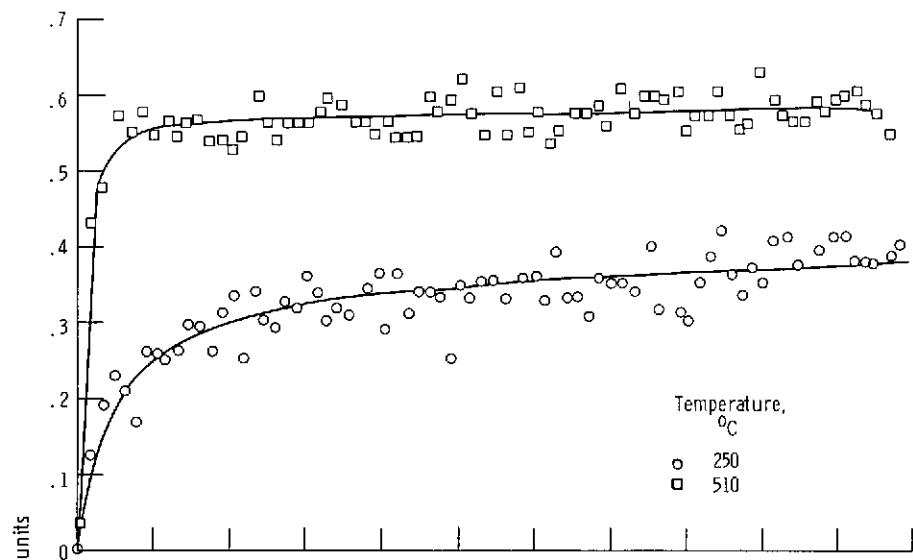
Figures 5 and 6 demonstrate the results of varying temperature. Figure 5 shows the results of heating the alloy at 250⁰, 490⁰, and 550⁰ C in oxygen at a pressure of 1×10^{-7} torr. Figure 5(a) indicates the growth of the aluminum oxide peak with time, and figure 5(b) indicates the decay of the 59-eV copper peak with time. Similarly, figures 6(a) and (b) show the same types of curves for temperatures of 250⁰ and 510⁰ C and a pressure of 5×10^{-6} torr. The trends shown in general on these curves indicate an increase in aluminum oxide in the surface region at a given time with increasing temperature, with the exception of the 550⁰-C, 1×10^{-7} -torr oxygen curves. In this case, the curves indicated oxide buildup at a rate higher than the lower temperature curves initially, but after 140 seconds the rate of film buildup decreased with time. This behavior was repeatable under the same conditions but did not occur at higher oxygen pressures.

Figure 7 shows the growth of the 520-eV oxygen Auger peak with time at room temperature and 550⁰ C at a pressure of 5×10^{-6} torr. As can be seen, there is an increased amount of oxygen in the surface region at 550⁰ C. These results give supporting evidence for temperature effects in the formation of an oxide layer, as indicated by the increased quantity of oxygen in the surface region (more than one layer sampled).

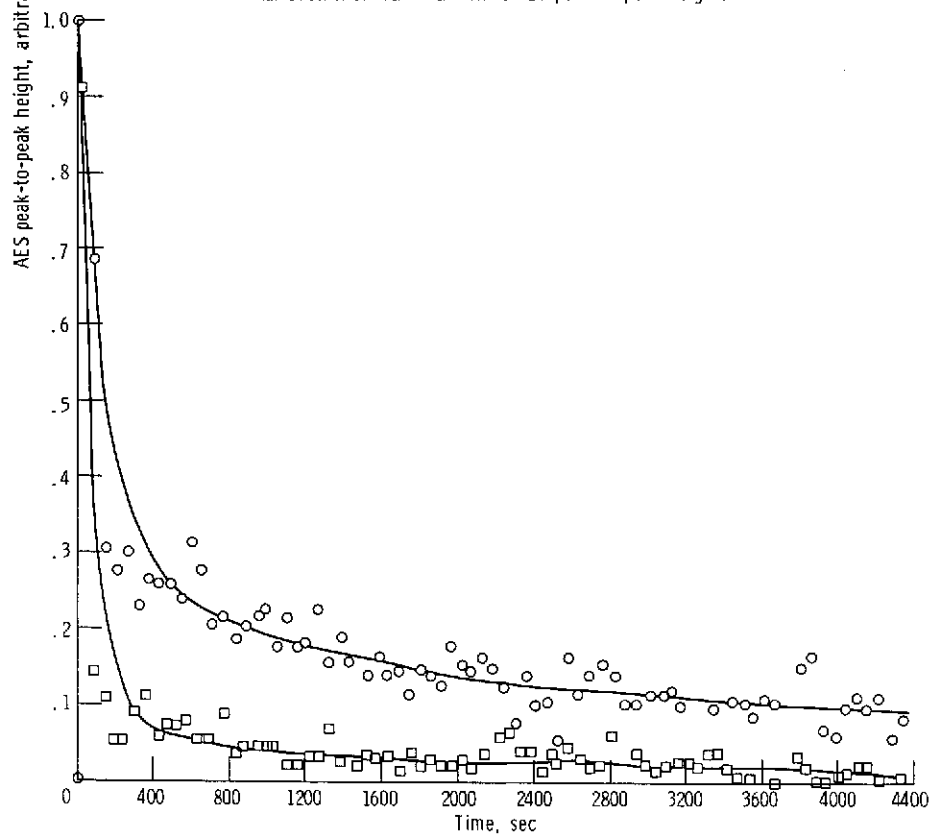
An attempt was made to separate the effect of thermal diffusion from effects of the presence of oxygen. The supply of oxygen was stopped, while the heating of the sample was continued. Figure 8 shows the results of terminating an oxygen exposure at 5×10^{-6} torr and 550⁰ C. As can be seen, the copper peak grows with time, which indicates diffusion of copper through the aluminum oxide surface layer. Examination of the low-energy AES spectrum under similar conditions showed that both copper and aluminum (no figure shown) have diffused through the surface layer. The temperature dependence of the film growth indicates that thermally activated diffusion plays an important part in the rate of film growth.

It is apparent that some additional mechanism must be operating to selectively cause a purely aluminum oxide layer, since both copper and aluminum diffusion can occur. If pure thermal diffusion were determining the film growth, then both copper and aluminum would be forming the surface oxide. This selective oxidation at low pressures has been observed previously (refs. 1 to 7). The mechanism is probably related to the higher reactivity of the aluminum, which provides a greater driving force for aluminum diffusion through the oxide layer, and the greater thermal stability of aluminum oxide. This result follows Kofstad's observation (ref. 1) that the less noble of the two metals forms the selective oxide.

The one exception to this behavior is the 550⁰ C, 1×10^{-7} torr case, which starts out with a higher oxidation rate as expected, but then reverses and indicates a decrease in thickness of the aluminum oxide layer. This alloy sample has phosphorus as a contaminant, which does not segregate on the surface rapidly until the sample is heated to approx-



(a) Growth of aluminum oxide AES peak-to-peak height.



(b) Decay of 59-eV copper AES peak-to-peak height.

Figure 6. - Oxidation of copper-aluminum alloy at 5×10^{-6} torr at various temperatures as a function of time.

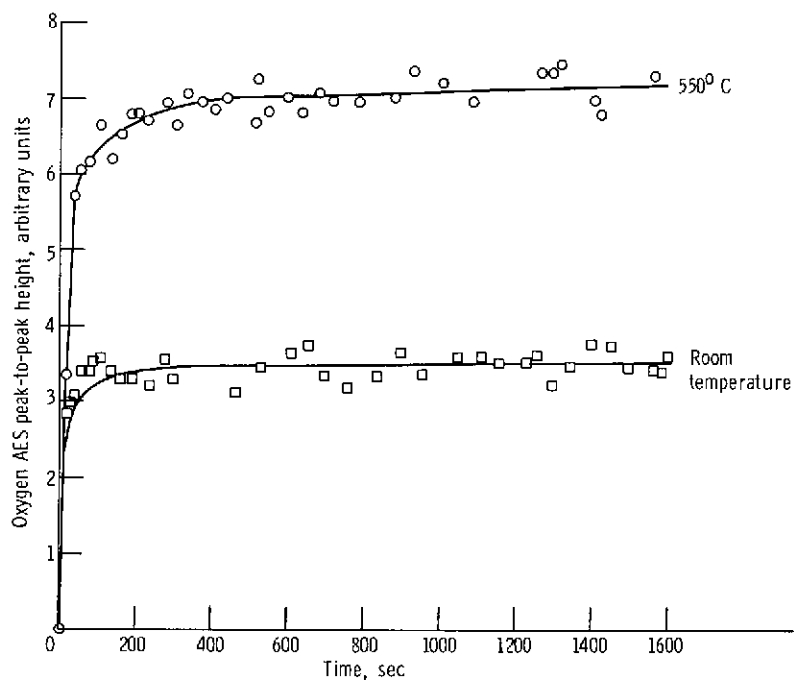


Figure 7. - Growth of 520-eV oxygen AES peak at an oxygen pressure of 5×10^{-6} torr for exposure at room temperature and at 550° C.

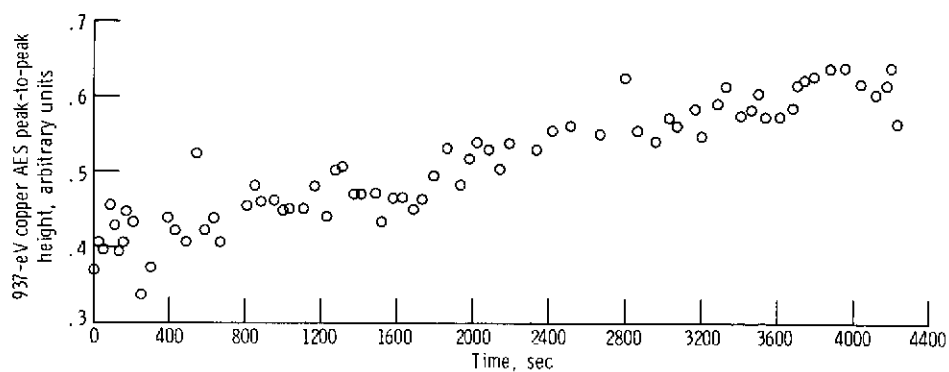


Figure 8. - Growth of 937-eV copper peak at 550° C and 5×10^{-6} torr after termination of oxidation.

imately 550° C. It seems possible that the phosphorus is interfering with the formation of the oxide, since it is unlikely that aluminum oxide is disassociating at 550° C. It is established in the literature (ref. 1) that addition of foreign atoms can either inhibit or enhance the growth of oxides. It is conceivable that the phosphorus can be behaving like an n-type donor and inhibiting the growth of the surface layer. At the higher pressures and temperatures, it is possible that volatile phosphorus-oxygen compounds can be formed, which limits the inhibiting effect of the phosphorus.

These results bear some relation to the phosphorus-inhibited studies. If figure 5 is examined for the 550°-C case, it can be seen that the increase in the copper 59-eV AES peak can be interpreted in terms of increased copper diffusion when the formation of the aluminum oxide layer is inhibited. These results therefore imply that the mechanisms for selective oxidation are controlled by the metal-oxide interface.

Pressure (Arrival Rate) Effects

In order to examine pressure effects, it is necessary to plot the data against exposure (number of atoms impinging on the surface per unit area per unit time). It can be seen that it would not be relevant to plot the data of figures 4 and 5 for the two pressures 1×10^{-6} and 5×10^{-6} torr on the same graphs, since five times as many oxygen atoms have impinged on the surface in the latter case in a given time interval. Therefore, if sufficient time were allotted, it is conceivable that the thickness in the slowly growing part of the 1×10^{-6} torr curves would approach that of the 5×10^{-6} torr curves. In order to examine whether the oxidation was arrival-rate limited, two conditions were imposed: exposure at 5×10^{-6} torr at a temperature of 510° C, and exposure at 1×10^{-6} torr at a temperature of 550° C (fig. 9). The figure shows that when the data are plotted on a comparable exposure scale, the slowly increasing part of the curve represents approximately the same thickness. In fact the 1×10^{-6} torr curve is slightly higher. If the oxidation were oxygen-arrival-rate limited rather than diffusion limited, a lower concentration would be expected at 1×10^{-6} torr.

There are two controlling rate phenomena in the formation of the oxide coating: diffusion and arrival rate. Either can limit the rate of oxide buildup. If exposures take place at sufficiently low pressures, the arrival-rate limiting conditions should be observable. For all of the conditions observed in this study (figs. 5, 6, and 8), the rate of oxide buildup was apparently diffusion limited rather than arrival-rate limited.

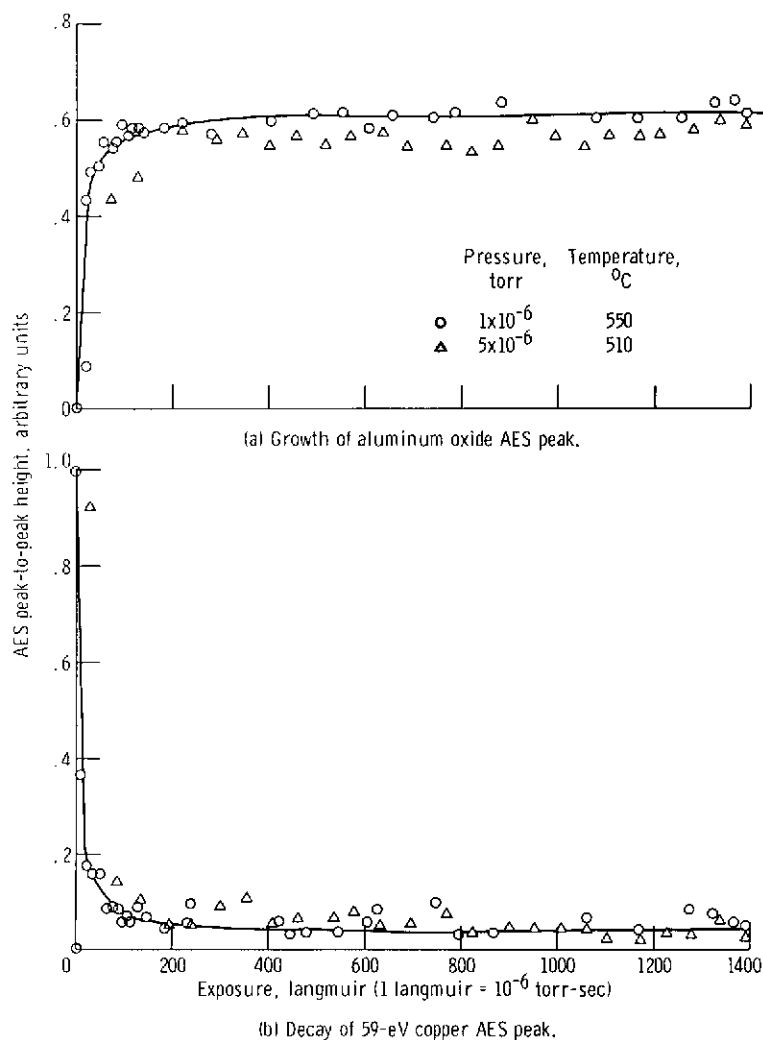


Figure 9. - Comparison of oxidation at 1×10^{-6} and 5×10^{-6} torr plotted on same exposure scale.

Functional Dependence of Film Growth

It is of interest to examine whether the growth of the oxide layer follows a specific model of growth rate. In performing this measurement, it is necessary to plot some parameter proportional to film thickness. The most logical quantity to plot is the growth of the aluminum oxide peak with time. There are several reasons, however, related to the nature of Auger spectroscopy for this not being the most desirable approach. First, the aluminum oxide peak is in a region of the spectrum where there are large background slopes, and in the initial stages of the growth, the structure of the spectrum is quite com-

plicated. This complicated structure introduces large errors in the true size of the peaks in the initial stages of growth. Second, AES is sampling several layers of the oxide with electrons originating from lower layers somewhat attenuated relative to the surface layer; therefore, the 55-eV aluminum oxide peak height is not a representation of layer thickness. Finally, the peak will saturate simply, because the range of sensitivity of AES is limited to a small number of layers. Because of these limitations, another approach was attempted which is similar to techniques used to obtain attenuation cross sections for low-energy electrons (ref. 17). This approach is to examine the attenuation of the high-energy (937 eV) copper peak with time. If the attenuation of the peak is a result of increasing film thickness, then the attenuation should have the relation

$$\frac{I}{I_0} = e^{-kx} \quad (1)$$

where I_0 is the peak height for the clean surface, I is the peak height after oxidizing for a time t , x is the film thickness, and k is the attenuation length. Therefore, the film thickness as a function of time should have the relation

$$x = -\frac{1}{k} \ln\left(\frac{I}{I_0}\right) \quad (2)$$

Therefore, plotting $-\ln(I/I_0)$ against time should give the film thickness in arbitrary units. This technique has several advantages. First, the high-energy copper peak appears in a region of relatively flat background. Second, if there is no copper in the covering layer, the attenuation is a good representation of the film thickness. Third, the high-energy electrons have a longer range in the oxide film and will enable detection to thicker layers (ref. 18). In fact, since the electrons have a longer range in oxide layers than in metals, the thicknesses could be substantial, possibly of the order of hundreds of angstroms.

In order to examine the growth rate, $\ln(I/I_0)$ was plotted against time. The data were then curve-fit by nonlinear least-squares analysis to the logarithmic growth curve given by

$$x = x_0 \ln\left(1 + \frac{t}{t_0}\right) \quad (3)$$

This relation should apply to the initial stages of oxidation (ref. 1). It has been derived from a number of different physical models, ranging from tunneling of electrons through

the film to crack formation in the oxide layer (ref. 7). At this point, no attempt will be made to select a specific model.

Figure 10 gives the curve fit to the logarithmic equation. A parabolic equation, $x = kt^{1/2}$ (ref. 1), which often applies for thicker oxide layers, was also curve fit to the data for comparison. As can be seen, the data follow the logarithmic equation. The fitting parameters obtained are $x_0 = 0.119$ (arbitrary units) and $t_0 = 0.129$ second. Therefore, these results follow the expected trends for the initial stages of oxidation.

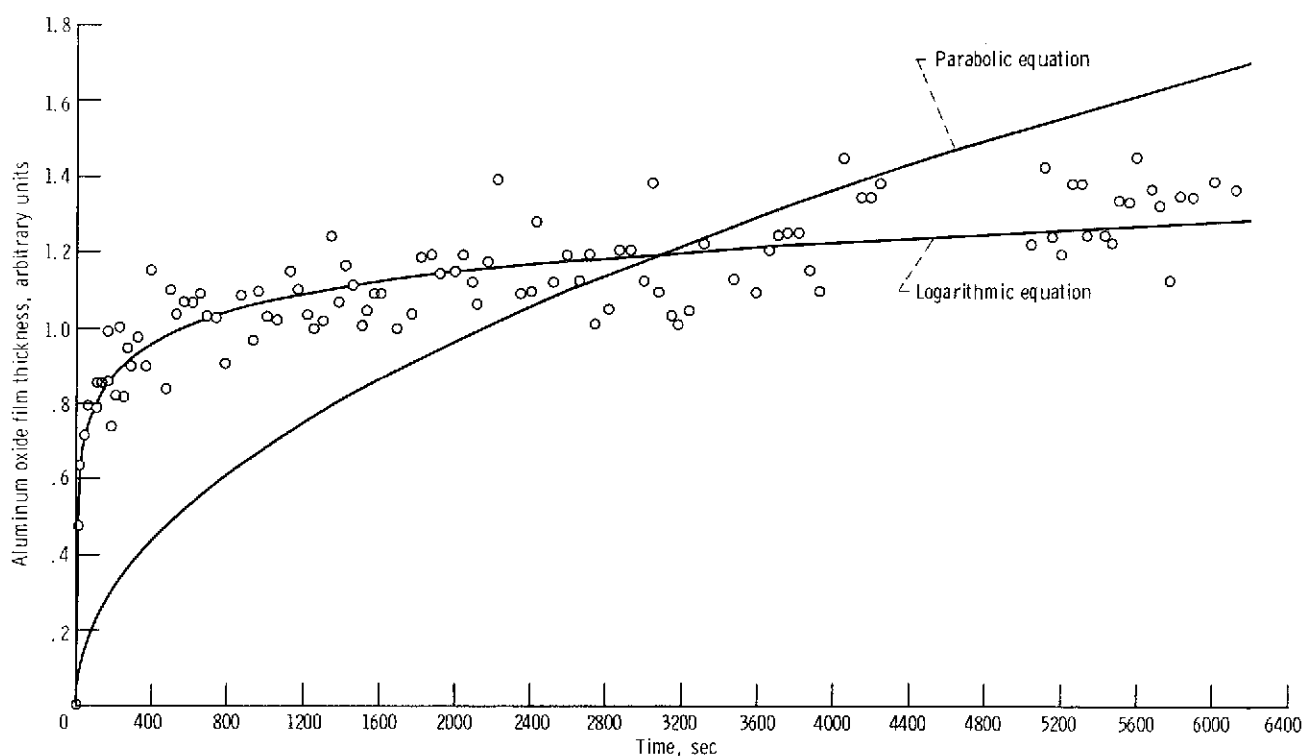


Figure 10. - Comparison of oxide film growth rate with growth curves given by logarithmic and parabolic equations. Temperature, 550° C; pressure, 5×10^{-6} torr.

Thickness of the Layer

It would be desirable to calibrate the thickness of the oxide layer. However, at this stage it is difficult to set a level for the thickness. Seah (ref. 17) obtained a thickness of approximately 8 monolayers for beryllium on copper by examining the 937-eV copper AES peak at an attenuation comparable to that of the 5×10^{-6} -torr oxidations. Therefore, the complete disappearance of the peak implies a considerably thicker layer. However,

beryllium is a metal, while aluminum oxide is an insulating layer. Reference 18 indicates that electron ranges may be much longer in insulators than in metals. Therefore, only a lower bound can be set on the thickness. It may be possible to perform controlled sputtering studies (refs. 12 and 13) in order to estimate film thicknesses. These will be performed in the future.

Practical Implications of Studies

The possibility of forming a thin oxide coating on surfaces may be practical from several standpoints. They may be capable of providing corrosion protection and resistance to wear. A problem would seem to exist with these thin films in that they may not self-heal. However, there is some possibility that this may not be as severe a problem as might be expected. Thick oxide scales exhibit spalling, since the metal-oxide interface has to maintain high stresses resulting from the change in crystal structure across the interface. There is evidence (refs. 19 and 20), however, that thin surface films can be extremely tenacious and may not fracture as easily as the thick films. Spalvins (ref. 19) has shown that sputter deposited gold films actually gave higher tensile strength to the substrate and that the substrate material could be drawn in tension without disrupting the gold film.

Therefore, it is conceivable that materials with thin oxide coatings would be beneficial from the standpoints of corrosion and wear. It would be worthwhile to produce surfaces with thin oxide coatings and perform friction and wear tests on them both in vacuum and in air in order to establish their tenacity.

SUMMARY OF RESULTS

A study was made of the initial stages of oxidation on a copper - 19.6-atomic-percent-aluminum alloy. The following are the principal results of the study:

1. Selective oxidation of the surface to an aluminum oxide layer on the alloy surface occurred.

2. The initial stages of oxidation followed a logarithmic growth curve $x = x_0 \ln \left(\frac{t}{\tau_0} \right)$.

By fitting the data with a nonlinear least-squares curve fit, the pre-logarithmic factor for the growth was found to be $x_0 = 0.119$ (arbitrary units), and the time constant for the growth was found to be $\tau_0 = 0.129$ second.

3. The surface was covered with an aluminum oxide film for all cases examined.

4. Complete disappearance of the 937-eV copper peak was obtained by heating at 700° C for 1 hour in oxygen at a pressure of 5×10^{-4} torr.

5. Studies of oxide growth at varying temperature and constant pressure indicated that thermally activated diffusion was important in oxide formation. However, some other physical mechanism was operating which promoted selective oxidation of the surface to aluminum oxide.

6. No strong pressure effect (arrival rate) was observed for pressures ranging from 1×10^{-7} to 5×10^{-4} torr.

Lewis Research Center,
National Aeronautics and Space Administration,
Cleveland, Ohio, September 7, 1973,
502-01.

REFERENCES

1. Kofstad, Per: High Temperature Oxidation of Metals. John Wiley & Sons, Inc., 1966.
2. Uhlig, H. H.: Structure and Growth of Thin Films on Metals Exposed to Oxygen. Corrosion Sci., vol. 7, no. 6, 1967, pp. 325-339.
3. Mrowec, S.: On the Mechanism of High Temperature Oxidation of Metals and Alloys. Corrosion Sci., vol. 7, no. 9, 1967, pp. 563-578.
4. Hauffe, Karl: Oxidation of Metals. Plenum Press, 1965.
5. Hauffe, Karl: The Mechanism of Oxidation of Metals and Alloys at High Temperatures. Progress in Metal Physics. Vol. 4. Bruce Chalmers, ed. Interscience Publ., 1953, pp. 71-104.
6. Kubaschewski, O.; and Hopkins, B. E.: Oxidation of Metals and Alloys. Butterworths Scientific Publ., 1953.
7. Uhlig, Herbert H.: Initial Oxidation Rate of Metals and the Logarithmic Equation. Acta Met., vol. 4, Sept. 1956, pp. 541-554.
8. Chang, Chuan C.: Auger Electron Spectroscopy. Surface Sci., vol. 25, 1971, pp. 53-79.
9. Ferrante, John; Buckley, Donald H.; Peper, Stephen V.; and Brainard, William A.: Use of LEED, Auger Emission Spectroscopy and Field Ion Microscopy in Microstructural Studies. NASA TM X-68152, 1972.
10. Wild, R. K.: Oxidation of Nimonic 80A at 800° C in Low Oxygen Pressures. Corrosion Sci., vol. 13, no. 2, Feb. 1973, pp. 105-112.

11. Suleman, M.; and Pattinson, E. B.: Observation of a Plasmon-Gain in the Fine Structure of the Aluminum Auger Spectrum. *J. Phys. F: Metal Phys.*, vol. 1, 1971, pp. L21-L24.
12. Ferrante, John: A Reply to "On the Measurement of Equilibrium Segregation Using Auger Electron Spectroscopy." *Scripta Met.*, vol. 5, no. 12, Dec. 1971, pp. 1129-1134.
13. Ferrante, John: An Auger Electron Spectroscopy and LEED Study of Equilibrium Surface Segregation in a Copper-Aluminum Alloy. *Acta Met.*, vol. 19, no. 8, Aug. 1971, pp. 743-748.
14. Ferrante, John: Auger Electron Spectroscopy Study of Surface Segregation in the Binary Alloys Copper-1 Atomic Percent Indium, Copper-2 Atomic Percent Tin, and Iron-6.55 Atomic Percent Silicon. NASA TN D-6982, 1973.
15. Jenkins, L. H.; and Chung, M. F.: LEED and Auger Investigations of a Cu(111) Surface. *Surface Sci.*, vol. 24, 1971, pp. 125-139.
16. Chang, Chuan C.: Low Energy Electron Diffraction Studies, Adsorption of O₂, CO, and N₂ on the Tungsten (112) Face. Ph.D. Thesis, Cornell Univ., 1967.
17. Seah, M. P.: Quantitative Auger Electron Spectroscopy and Electron Ranges. *Surface Sci.*, vol. 32, 1972, pp. 703-728.
18. Helms, C. R.; and Spicer, W. E.: Comparison of the Oxidation Process in Strontium and Cerium by Ultraviolet Photoelectron Spectroscopy. *Appl. Phys. Letters*, vol. 21, no. 5, Sept. 1, 1972, pp. 237-239.
19. Spalvins, Talivaldis: Characteristics of Ion Plated Films Including Mechanical Properties and Lubrication. *Sputtering and Ion Plating*. NASA SP-5111, 1972, pp. 41-57.
20. Tingle, E. D.: The Importance of Surface Oxide Films in the Friction and Lubrication of Metals. *Trans. Faraday Soc.*, vol. 46, 1950, pp. 93-102.